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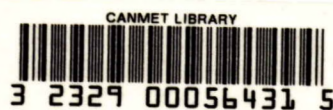
MODELING PULVERIZED COAL-WATER SLURRY COMBUSTION

Z.Q. Zhou and K. V. Thambimuthu

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Z.Q. Zhou,
Department of Chemical Engineering,
Queens University,
Kingston, Ontario, Canada.

K.V.Thambimuthu,
Energy Research Laboratories,
Canada Centre for Mineral and Energy Technology,
Energy Mines and Resources,
Ottawa, Canada.

1. INTRODUCTION

Coal-water slurries(CWS) appear attractive as replacement fuel for heavy oil and pulverized coal in industrial and utility boilers. Numerous pilot and demonstration trials have been undertaken during the last decade. However, the bulk of this work has concentrated on the ignition stability of flames in burners, atomization, and in evaluating erosion and derating in compact oil-designed boilers.

The solids loading in CWS is usually around 70 wt%. The balance made up of water not only consumes energy for evaporation, but also delays the subsequent ignition of the volatiles released from the coal. It is estimated that the enthalpy for moisture evaporation usually contributes to a 3-5% loss in the heating value^(1,2) of the fuel. Besides these factors, and due to the presence of multiple coal particles in individual droplets, it is well known⁽¹⁻⁶⁾ that the coal particles agglomerate and swell during devolatilization. In view of this, the processes of ignition, volatile and char combustion may be somewhat different^(5,6) from those observed for pulverized coal. Thus, there appears to be compelling need to better understand the phenomena, if not for the purpose of promoting the wider use of CWS in various combustion applications.

2. BACKGROUND

The approach adopted when modeling coal combustion assumes that the combustion process occurs in several sequential steps with little or no overlap between the various stages. The respective stages are assumed to be moisture evaporation, devolatilization and gaseous combustion, and heterogeneous char burnout. For conventional pulverized coal and fluidized bed combustion, the evaporation of water is either ignored or considered to be instantaneous. As mentioned previously, this stage cannot be ignored for CWS due to the high moisture content. Furthermore, droplets tend to carry multiple coal particles. The modeling of CWS droplets may thus centre on water evaporation and agglomeration, and there is no equivalent analogy to these phenomena in models developed for the pulverized or fluidized bed combustion of coal.

Water Evaporation

Two approaches may be used to model water evaporation. The first one assumes external surface evaporation, i.e., the water evaporates only at the outer boundary or surface of the CWS droplets. The vapour produced then diffuses through the stagnant gas film surrounding the droplet. Interstitial water in the CWS droplet replenishes that lost at the external surface, and continues until complete drying occurs. A number of workers^(2,4,5) have adopted this concept in the literature. The boiling temperature of water was generally assumed to be the evaporation temperature at the external surface⁽²⁾. However, the wet bulb or saturation temperature is also adopted as the equilibrium temperature at the evaporation surface in some instances^(4,5).

The second treatment considers internal surface evaporation, i.e., a two zone model. As evaporation progresses, a receding internal evaporation front gradually moves towards the droplet core and simultaneously creates a dry outer shell. Heat from the environment external to the dry shell is transferred by conduction to the internal evaporation interface. During this process, the dry shell increases in temperature and acts as a pathway for vapour diffusion to the gas phase surrounding the external droplet surface. This model appears to have gained more widespread favour. Reference 3 for instance has simplified this model with a pseudo-steady state assumption for the dry zone, while reference 7 assumed no heat loss in the dry zone. The model also permits simultaneous coal devolatilization as the temperatures increase in the dry zone. In many respects, the latter approach serves as a much more realistic description of CWS droplet combustion (15).

Devolatilization.

A considerable amount of work has been undertaken on the devolatilization kinetics of coal at fast heating rates. A number of kinetic models have also been proposed. The basic premise of all these models is that the pyrolysis of coal is temperature dependent, and hence the models are equally applicable to CWS droplets. The kinetic model for devolatilization in references 4 and 5 were expressed as an overall reaction model similar to that first proposed by Badzioch(8). Reference 3 assumes two competing first order reactions similar to that proposed by Sticker et. al.(9). A common feature of the various models is that the temperature history must be specified before the devolatilization rate may be calculated. This implies that the equations are closely coupled to the heat and mass transfer processes.

Char Residue Combustion.

For pulverized coals, the char residue reaction is assumed to be heterogeneous. In most cases it is also assumed that the oxidation of carbon to CO is the dominant product at the char surface. The carbon monoxide further oxidizes in the gas phase, and the reaction is catalysed by moisture present in the gas phase. The homogeneous gas phase reaction is usually very rapid, and the CO reaction at the char surface is assumed to be the rate limiting step. For conventional dry pulverized coal combustion, Walker(11) has shown the char-water reaction can be effectively ignored.

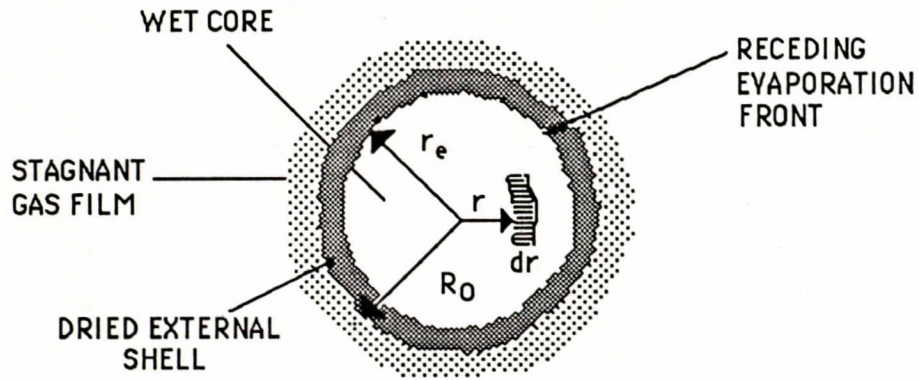
As is common for most heterogeneous reactions, char combustion is controlled by the chemical, bulk, or pore diffusion limited reaction rate. The dominance of one or other of these regimes being determined by particle size and morphology, the prevailing temperature, and heat and mass transfer rates. The greatest difference between pulverized and CWS char combustion will probably arise from the morphology (due to swelling, agglomeration and fragmentation) of the CWS char particles(15). These changes normally influence the overall reaction rate through one or other of the limiting regimes identified previously.

In models for CWS, reference 2 assumed that char oxidation was bulk diffusion controlled and adopted Field's formula(10) for the overall rate expression. References 3 and 4 on the other hand assume pore diffusion to be limiting. Most of the experiments with coarse CWS droplets, have shown that pore diffusion is the dominant reaction regime(15) for char combustion.

3. THE COMBUSTION MODEL FOR CWS

For simplicity, the CWS droplets are assumed to be spherical with a uniform composition and properties. Combustion is also assumed to occur in a gaseous environment without any limitations in the oxygen content.

Figure 1. Schematic of an Evaporating CWS Droplet



Evaporation

The two zone model is assumed for moisture evaporation as shown in Figure 1. In order to simplify the mathematical treatment the temperature at the internal evaporation surface is assumed to be constant, and the wet core temperature is also assumed to remain at its initial value. The equation for energy conservation at the internal evaporation surface is;

$$4\pi r_e^2 \rho_s W L dr_e = -4\pi r_e^2 \lambda_s (\delta T / \delta r) |_{r_e} dt \quad (1)$$

which rearranges to;

$$(dr_e/dt) = -(\lambda_s / \rho_s W L) (\delta T / \delta r) |_{r_e} \quad (2)$$

The evaporation rate at the internal surface may be defined as;

$$K_w = (dG_w / 4\pi r_e^2 dt) = \rho_s W (dr_e/dt) \quad (3)$$

which with substitution of equation 2 becomes;

$$K_w = -(\lambda_s / L) (\delta T / \delta r) |_{r_e} \quad (4)$$

The temperature gradient in the dry zone may be found by solving an energy balance. In this instance, heat conduction is assumed in the dry zone;

$$(1/a)(\delta T / \delta t) = (\delta^2 T / \delta r^2) + (2/r)(\delta T / \delta r) \quad (5)$$

with an initial boundary condition:

$$t=0; T(0,r) = T_0 = \text{constant} \quad (6)$$

and other boundary conditions;

$$r=R_0; -\lambda_s (\delta T / \delta r) |_{R_0} = \alpha(T_g - T |_{R_0}) + \sigma \epsilon (T_w^4 - T |_{R_0}^4) \quad (7)$$

$$r=r_e; T(t,r_e) = T_0 = \text{constant} \quad (8)$$

The general solution for equation 5 may be written as;

$$T = T (R_0, r, r_e, t) \quad (9)$$

where R_0 and r_e are variables. From a derivative of the temperature with respect to the radius, and equations 3 and 4, the time for moisture evaporation is given by;

$$t_w = -(\rho_s W L / \lambda_s) \int_{R_0}^0 (\delta T / \delta r) |_{r_e} dr_e \quad (10)$$

The amount of moisture evaporated in a time interval dt may be written as

$$dG = -4\pi r_e^2 dr_e \rho_s W \quad (11)$$

which with substitution of equation 4 and integration becomes;

$$G_w |_t = -(4\pi \lambda_s / L) \int_0^t r_e^2 \{ \delta T(r,t) / \delta r \} |_{r_e} dt \quad (12)$$

and represents the total amount of water evaporated at any time t .

Devolatilization

Devolatilization is assumed to occur at a steady particle temperature. This simplification being justified because particle heating occurs in a time scale an order of magnitude less than that required for devolatilization. A simple overall first order rate expression with an Arrhenius type temperature dependence is also assumed. Thus,

$$K_V = (dV/dt) = -(V-V_f)A_V \exp\{-E_V/RT_p\} \quad (13)$$

or

$$(dG_V/dt) = -(V-V_f)G_0 A_V \exp\{-E_V/RT_p\} \quad (14)$$

A model for devolatilization should also predict the composition and heating value of the volatiles. These are often dependent on the coal type, and in the case of CWS, the heating value changes due to the simultaneous evolution of residual moisture. The devolatilization rates and compositions also depend on the thermal history of the droplet. These features are difficult to ameliorate. In the absence of other models able to represent these trends, a simple model similar to the one proposed above with an assumed mean heating value for the volatiles is used.

Combustion of Char Residue

A first order reaction with respect to the oxygen concentration is assumed, with CO as the primary reaction product at the char surface. The kinetic model essentially follows that proposed by Field(12). Char oxidation is assumed to be pore diffusion controlled (i.e diffusion and chemical kinetics) and is given by;

$$K_C = \{f P_O / [(1/\xi k_C) + (1/\beta)]\} \quad (15)$$

where the rate expression is again defined by an Arrhenius relationship;

$$k_C = A_C \exp\{-E_C/RT_p\} \quad (16)$$

The amount of char consumed by oxidation is;

$$dG_C = -4\pi R_0^2 K_C \quad (17)$$

The factor f in equation 15 varies from 0.375-0.75 kg carbon/kg of oxygen being dependent on the CO/CO₂ ratio. ξ is a correction factor for the particle reaction area, and is influenced by swelling/agglomeration of the slurry droplet.

Energy Conservation Equation

The average temperature of the dried agglomerate is used to calculate the devolatilization and char combustion rates. This simplifying assumption is justified by the observation that the rate of devolatilization and char burnout are likely to be much slower than the particle heat up rate. The energy balance equation may be written as follows;

$$(1/3)R_0\rho_s C_{ps}(dT_p/dt) = \alpha(T_g - T_p) + \sigma\varepsilon(T_w^4 - T_p^4) + K_C H_C \quad (18)$$

The initial boundary condition is taken as the average temperature of the CWS droplet when evaporation ends; this temperature is obtained from a solution of equation 5.

Convective Heat and Mass Transfer

The Ranz-Marshall correlation may be used to calculate the heat and mass transfer coefficients. These are;

$$Nu = (2\alpha R_0/\lambda_g) = 2 + 0.69Re^{0.5} Pr^{0.33} \quad (19)$$

$$Sh = (2\beta R_0/D_g) = 2 + 0.69Re^{0.5} Sc^{0.33} \quad (20)$$

The above expressions are usually coupled with momentum transfer equations established for the system being modeled.

4. SPECIAL FEATURES

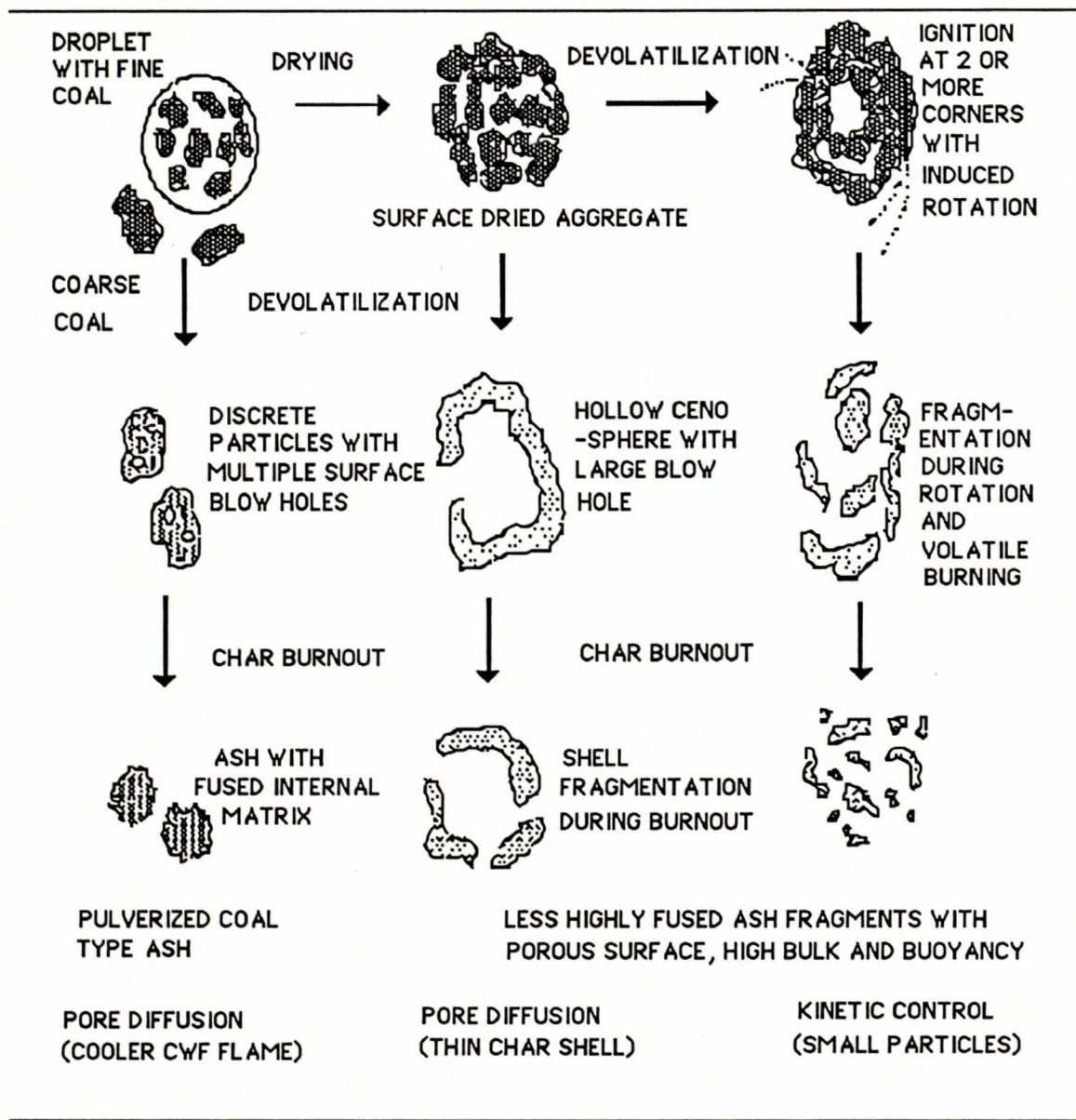
The Morphology of CWS Char Particles

During the devolatilization stage the CWS droplets swell due to the agglomeration of coal particles. This swelling behaviour appears to be a function of the coal type and its swelling index. However, unlike conventional pulverized coals, swelling also appears to be a characteristic feature of CWS droplet combustion⁽¹⁵⁾. This behaviour probably stems from increased volatile evolution in both the moisture drying and devolatilization stages, that tends to promote a greater degree of swelling in the agglomerated coal particles (relative to the behaviour observed during pulverized combustion of the same coal).

The impact of the above is that CWS droplets form large hollow char cenospheres whose surface may be additionally porous. Thus, char oxidation within and external to the particle surface is more likely controlled by pore diffusion. This and other modes of char combustion for CWS identified in a recent review⁽¹⁵⁾ are summarized in Figure 2. The three modes of char burnout which originate from the coarse coal and aggregated fine coal droplets found in CWF sprays⁽¹⁵⁾, indicate that char combustion is dominated by pore diffusion, and perhaps kinetic control when the char particles fragment. The model developed for char combustion must be cognizant of the above effects. The correction for the char morphology may be introduced by

selecting an appropriate value for the reaction area term ξ , or preferably by adopting alternate geometric models (currently assumed to be a shrinking sphere) for the char combustion regime.

Figure 2. Mechanism of CWS Combustion



Other Considerations

The validity of the assumption of a constant equilibrium temperature at the evaporation interface merits some comment. The temperature history of a suspended CWS droplet has been measured by two thin thermocouples inserted at different radial locations⁽¹³⁾. The temperatures at these two locations showed similar profiles, but the equilibrium temperatures differed somewhat. The equilibrium temperature was generally higher near the external surface due to its location in a heat conduction zone. Reference 14 calculated the equilibrium temperatures for droplets at various furnace temperatures (or heating rates) in 1000-1606 K range, and found a

70 variation in the temperatures (342-349 K). These results also showed close agreement with the experimental measurements.

Concerning the degree of overlap between the devolatilization and char combustion regimes, reference 1 reported a 90 % weight loss of volatiles, and 10 wt% of fixed carbon for a bituminous CWS at the end of the volatile combustion phase. However, these values are also dependent on the coal type, heating rates, and the volatile content. Thus, a parallel competing reaction model for devolatilization and char burnout may be appropriate in some instances.

5. CONCLUSIONS

Based on a review of the technical literature, a simple model more cognizant of recent findings on the mechanism of CWS combustion has been proposed. The evaporation process is separated from two subsequent processes, i.e., devolatilization and char combustion. The evaporation rate at a shrinking interface is solved from an energy balance equation in the dry zone. Devolatilization is modeled using a simple overall rate expression. Some overlap in the devolatilization and moisture evaporation regime is also assumed. The oxidation of the char residue is assumed to be controlled by mass transfer and the reaction kinetics (i.e. pore diffusion), the latter with a first order dependence on the oxygen concentration. The influence of swelling/agglomeration on the combustion behaviour of CWS droplets is modeled by introducing a correction factor to the reaction area term in the char combustion regime.

In view of the complex influence of coal properties, swelling and agglomeration of the CWS droplets, this model has not been evaluated. Experiments are in progress to elucidate these effects, and the results will be compared with the model predictions at a future date.

NOMENCLATURE

a	Thermal diffusivity.
A_v, A_c	Frequency factor in the Arrhenius rate equations for devolatilization and char combustion.
C_{ps}	Specific heat capacity.
D_g	Vapour diffusion coefficient.
E_v, E_c	Activation energy for devolatilization and char combustion.
f	Ratio of carbon monoxide to carbon dioxide gas concentration.
G_o	Initial weight, other subscripts for water, volatiles and char.
dG	Incremental weight.
H_c	Heat of reaction for char combustion.
K_w, K_v, K_c	Rate of moisture evaporation, volatile evolution and char combustion.
k_c	Reaction rate constant for char combustion
L	Latent heat of evaporation.
P_o	Concentration of oxygen
Pr	Prandtl Number
R	Universal gas constant.
Re	Reynolds Number
R_o	Initial droplet radius.
r	Particle or droplet radius
r_e	Radius of the moisture evaporation front.
Sc	Schmidt Number
T, T_p	Transient and average temperature of the dry zone.
T_g, T_w	Temperature of gas and furnace wall.
t	Time.
V, V_f	Transient and final volatile content.

W	Moisture content in CWS
Greek	
α	Convective heat transfer coefficient
β	Convective mass transfer coefficient.
ε	Emissivity of a particle.
λ_g, λ_s	Conductivity of gas, dried solids phase.
ξ	Correction factor for the reaction area.
ρ_s	Density of the droplet.
σ	Radiation constant.

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